PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KYOTO UNIV

(72)Inventor : YOSHIDA JUNICHI
ITAMI KENICHIRO

(54) MULTI-SUBSTITUTED PYRIMIDINE AND METHOD FOR SELECTIVELY PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a selective method for producing a multi-substituted pyrimidine suitable for a luminescent material, etc.

SOLUTION: This selective method for producing the multi-substituted pyrimidine is provided by reacting a first π-electron-containing compound containing the first π-electron-containing group with a first carbon atom in the 2 carbon atoms positioned at meta-positions for an organic group in a pyrimidine bonded with the organic group containing an atom selected from group 13-16 elements on a long period type periodic table of elements for bonding the first π-electron-containing group, reacting a second π-electron-containing compound with a second carbon atom for bonding the second π-electron-containing group and then substituting the organic group with a third π-electron-containing group by reacting the third π-electron-containing compound containing the third π-electron-containing group. It is preferable to have an aspect of selecting the first to third π-electron-containing groups from aryl, heteroaryl, alkenyl and alkynyl groups and an aspect of using a cross coupling reaction as the substitution reaction of the organic group with the third π-electron-containing group.

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* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]
It can set to the pyrimidine which the organic radical containing the atom chosen from the 16th group combined through this atom from the 13th group in the long period mold periodic table of an element,
After having made the first pi electron content compound containing the first pi electron content radical react to the first carbon atom of the two carbon atoms located in the meta position to this organic radical, having combined this first pi electron content radical, making the second pi electron content compound containing the second pi electron content radical react to the second carbon atom and combining this second pi electron content radical,
The alternative manufacture approach of the multi-permutation pyrimidine characterized by making the third pi electron content compound which contains the third pi electron content radical for said organic radical react, and making it permute by this third pi electron content radical.
[Claim 2]
The alternative manufacture approach of a multi-permutation pyrimidine according to claim 1 that atoms are either S atom, Si atom, Se atom, O atom, germanium atom, Sn atom, Pb atom and a B atom.
[Claim 3]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-2 as which the first pi electron content radical, the second pi electron content radical, and the third pi electron content radical are chosen from an aryl group, a hetero aryl group, an alkenyl radical, and an alkynyl group.
[Claim 4]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-3 which are the metal salts in which the first pi electron content compound and the second pi electron content compound contain an aryl group, a hetero aryl group, an alkenyl radical, and the pi electron content radical chosen from an alkynyl group.
[Claim 5]
The alternative manufacture approach of a multi-permutation pyrimidine according to claim 4 that a metal salt is lithium salt.
[Claim 6]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-5 to which the reaction which combines the first pi electron content radical to the first carbon atom, and the reaction which combines the second pi electron content radical to the second carbon atom are performed using a catalyst.
[Claim 7]
The alternative manufacture approach of a multi-permutation pyrimidine according to claim 6 that a catalyst contains 2, 3-dichloro -5, and the 6-dicyano-1, 4-benzoquinone.
[Claim 8]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-7 to which the reaction which combines the second pi electron content radical with the second carbon atom is performed using the catalyst and reaction container which were used on the occasion of the reaction which combines the first pi electron content radical with the carbon atom of this first.
[Claim 9]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-8 combined with

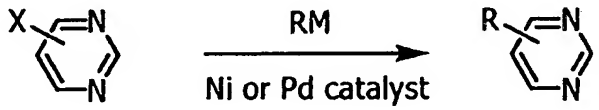
the carbon atom of the 2nd place with which an organic radical adjoins two nitrogen atoms in a pyrimidine ring.
[Claim 10]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-9 whose reactions which the third pi electron content compound which contains the third pi electron content radical for an organic radical is made to react, and are made to permute by this third pi electron content radical are cross coupling (Cross-Coupling) reactions.
[Claim 11]
The alternative manufacture approach of a multi-permutation pyrimidine according to claim 10 that a cross coupling (Cross-Coupling) reaction is performed under existence of a metal catalyst.
[Claim 12]
The alternative manufacture approach of a multi-permutation pyrimidine according to claim 11 that a metal catalyst is a nickel catalyst.
[Claim 13]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-12 which are the magnesium content halogenides in which the third pi electron content compound contains an aryl group, a hetero aryl group, an alkenyl radical, and the pi electron content radical chosen from an alkynyl group.
[Claim 14]
The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-13 whose multi-permutation pyrimidines are pyrimidines in a pyrimidine ring which the pi electron content radical permuted by the carbon atom of the location of the 2nd place, the 4th place, and the 6th place.
[Claim 15]
(1) The first pi electron content compound, the second pi electron content compound, and the third pi electron content compound are univalent compounds. (2) The first pi electron content compound and the second pi electron content compound are univalent compounds. The first pi electron content compound and the third pi electron content compound are univalent compounds. (3) whose third pi electron content compound is a divalent compound -- The first pi electron content compound is a univalent compound. (4) whose second pi electron content compound is a divalent compound -- The second pi electron content compound and the third pi electron content compound are divalent compounds. (5) The first pi electron content compound is a divalent aryl compound, and the second pi electron content compound and the third pi electron content compound are univalent aryl compounds. (6) The first pi electron content compound and the third pi electron content compound are divalent aryl compounds. The first pi electron content compound and the second pi electron content compound are divalent aryl compounds. the list whose second pi electron content compound is a univalent aryl compound -- (7) -- The alternative manufacture approach of a multi-permutation pyrimidine given in either of claims 1-14 of ** whose third pi electron content compound is a univalent aryl compound which are either at least.
[Claim 16]
The multi-permutation pyrimidine characterized by being manufactured by the alternative manufacture approach of the multi-permutation pyrimidine a publication by either of claims 1-15.
[Claim 17]
The multi-permutation pyrimidine according to claim 16 which a pi electron content radical comes to permute by the carbon atom of the location of the 2nd place in a pyrimidine ring, the 4th place, and the 6th place.

[Translation done.]

DETAILED DESCRIPTION

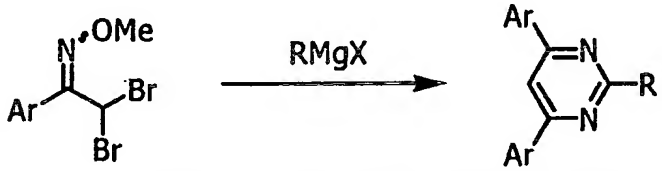
[Detailed Description of the Invention]
[Field of the Invention]
[0001]
This invention relates to the agonist antagonist of an estrogen receptor, the multi-permutation pyrimidine suitable as a luminescent material etc. for various fields, and its efficient alternative manufacture approach.
[Background of the Invention]
[0002]
The agonist antagonist of an estrogen receptor, and since it is promising as [luminescent material] especially, as for the multi-permutation pyrimidine, development of the alternative and efficient synthetic approach is desired.
In the former, introducing a substituent into a pyrimidine is known by the cross coupling reaction expressed with the following scheme, for example.
[Formula 1]

Cross-Coupling



moreover, the alkyl nature ring closure expressed with the following scheme -- cyclization of a pyrimidine -- introducing a substituent into a pyrimidine using composition is known (nonpatent literature 1 reference).
[Formula 2]

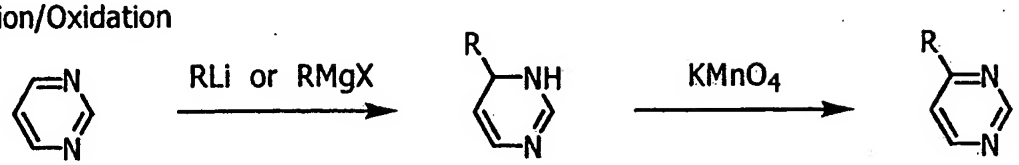
Alkylative Annulation



Kakiya, H.; Yagi, K.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2002, 124,** 9032.

Moreover, introducing a substituent into a pyrimidine is known by the addition and the oxidation reaction expressed with the following scheme (nonpatent literature 2 reference).
[Formula 3]

Addition/Oxidation



Bredereck, H.; Gompper, R.; Herlinger, H. *Angew. Chem.* 1958, *70*, 571.

However, the introductory location of a substituent cannot be controlled in these cases, but there is a problem that a desired multi-permutation pyrimidine is efficiently [alternatively and] uncompoundable.

[0003]

[Nonpatent literature 1] Kakiya,H.;Yagi,K.;Shinokubo,H.;Oshima,K., J.Am.Chem.Soc.2002,124,9032

[Nonpatent literature 2] Bredereck,H.Gompper,R.;Herlinger,H., Angew.Chem.1958,70,571

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0004]

This invention solves said problem in the former, and makes it a technical problem to attain the following purposes. Namely, this invention aims at offering the agonist antagonist of an estrogen receptor, the multi-permutation pyrimidine suitable as a luminescent material etc. for various fields, and its efficient alternative manufacture approach.

[Means for Solving the Problem]

[0005]

In order to solve said technical problem, as a result of this invention persons' inquiring wholeheartedly, knowledge [that a desired multi-permutation pyrimidine is alternatively compoundable efficiently] was acquired by introducing a pi electron content radical into the carbon atom located in the meta position to the substituent permuted by the pyrimidine ring, and making said substituent permute by the pi electron content radical after that. Based on said knowledge according [this invention] to this invention persons, said The means for solving a technical problem is as follows. namely

<1> It can set to the pyrimidine which the organic radical containing the atom chosen from the 16th group combined through this atom from the 13th group in the long period mold periodic table of an element,

After having made the first pi electron content compound containing the first pi electron content radical react to the first carbon atom of the two carbon atoms located in the meta position to this organic radical, having combined this first pi electron content radical, making the second pi electron content compound containing the second pi electron content radical react to the second carbon atom and combining this second pi electron content radical,

It is the alternative manufacture approach of the multi-permutation pyrimidine characterized by making the third pi electron content compound which contains the third pi electron content radical for said organic radical react, and making it permute by this third pi electron content radical.

<2> An atom is the alternative manufacture approach of a multi-permutation pyrimidine given in the above <1> which is either S atom, Si atom, Se atom, O atom, germanium atom, Sn atom, Pb atom and B atom.

<3> The first pi electron content radical, the second pi electron content radical, and the third pi electron content radical are the alternative manufacture approaches of olefin joint two or more content compound given in either of <2> from the above <1> chosen from an aryl group, a hetero aryl group, an alkenyl radical, and an alkynyl group.

<4> The first pi electron content compound and the second pi electron content compound are the alternative manufacture approaches of a multi-permutation pyrimidine given in either of <3> from the above <1> which is a metal salt containing an aryl group, a hetero aryl group, an alkenyl radical, and the pi electron content radical chosen from an alkynyl group.

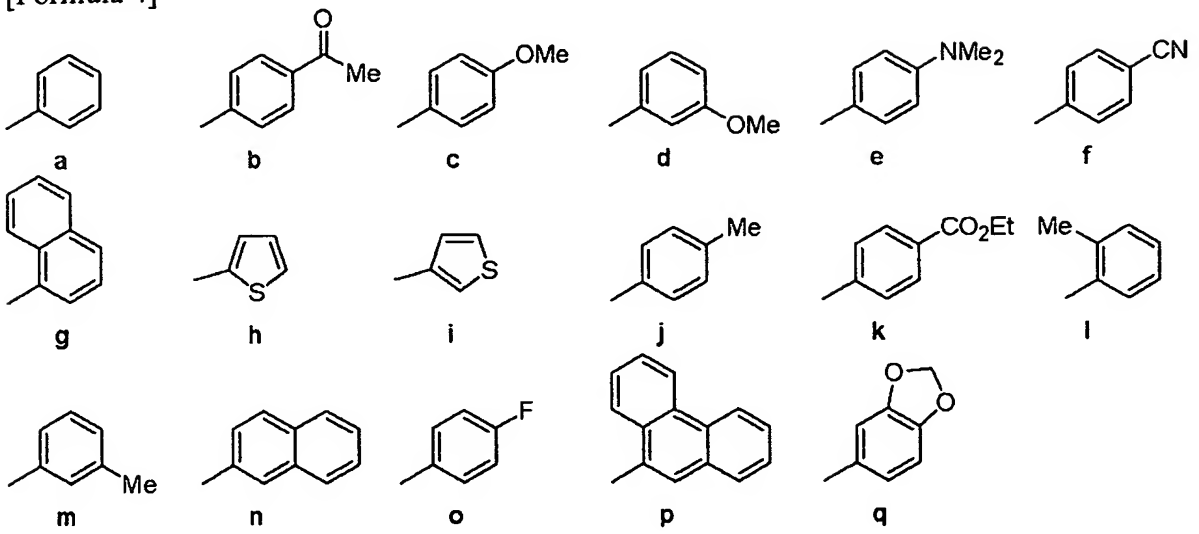
<5> A metal salt is the alternative manufacture approach of a multi-permutation pyrimidine given in the above <4> which is lithium salt.

<6> The reaction which combines the first pi electron content radical to the first carbon atom, and the reaction which combines the second pi electron content radical to the second carbon atom are the alternative manufacture approaches

of a multi-permutation pyrimidine given in either of <5> from the above <1> performed using a catalyst.
<7> A catalyst is the alternative manufacture approach of a multi-permutation pyrimidine given in the above <6> containing 2, 3-dichloro -5, and the 6-dicyano-1, 4-benzoquinone.
<8> The reaction which combines the second pi electron content radical with the second carbon atom is the alternative manufacture approach of olefin joint two or more content compound given in either of <7> from the above <1> performed using the catalyst and reaction container which were used on the occasion of the reaction which combines the first pi electron content radical with the carbon atom of this first.
<9> An organic radical is the alternative manufacture approach of a multi-permutation pyrimidine given in either of <8> from the above <1> combined with the carbon atom of the 2nd place contiguous to two nitrogen atoms in a pyrimidine ring.
<10> The reaction which the third pi electron content compound which contains the third pi electron content radical for an organic radical is made to react, and is made to permute by this third pi electron content radical is the alternative manufacture approach of a multi-permutation pyrimidine given in either of <9> from the above <1> which is a cross coupling (Cross-Coupling) reaction.
<11> A cross coupling (Cross-Coupling) reaction is the alternative manufacture approach of a multi-permutation pyrimidine given in the above <10> performed under existence of a metal catalyst.
<12> A metal catalyst is the alternative manufacture approach of a multi-permutation pyrimidine given in the above <11> which is a nickel catalyst.
<13> The third pi electron content compound is the alternative manufacture approach of a multi-permutation pyrimidine given in either of <12> from the above <1> which is a magnesium content halogenide containing an aryl group, a hetero aryl group, an alkenyl radical, and the pi electron content radical chosen from an alkynyl group.
<14> It is the alternative manufacture approach of a multi-permutation pyrimidine given in either of the above <1> whose multi-permutation pyrimidine is a pyrimidine which the pi electron content radical permuted by the carbon atom in a pyrimidine ring with which it is located in the 2nd place, the 4th place, and the 6th place to <13>.
<15> (1) The first pi electron content compound, the second pi electron content compound, The first pi electron content compound and the second pi electron content compound are univalent compounds. (2) whose third pi electron content compound is a univalent compound -- [and] The first pi electron content compound and the third pi electron content compound are univalent compounds. (3) whose third pi electron content compound is a divalent compound -- The first pi electron content compound is a univalent compound. (4) whose second pi electron content compound is a divalent compound -- The second pi electron content compound and the third pi electron content compound are divalent compounds. (5) The first pi electron content compound is a divalent aryl compound, and the second pi electron content compound and the third pi electron content compound are univalent aryl compounds. (6) The first pi electron content compound and the third pi electron content compound are divalent aryl compounds. The first pi electron content compound and the second pi electron content compound are divalent aryl compounds. the list whose second pi electron content compound is a univalent aryl compound -- (7) -- The third pi electron content compound is the alternative manufacture approach of a multi-permutation pyrimidine given in either of <14> from the above <1> of ** which is a univalent aryl compound which is either at least.
<16> It is the multi-permutation pyrimidine characterized by being manufactured by the alternative manufacture approach of the multi-permutation pyrimidine a publication from the above <1> by either of <15>.
<17> It is a multi-permutation pyrimidine given in the above <16> which a pi electron content radical comes to permute by the carbon atom in a pyrimidine ring located in the 2nd place, the 4th place, and the 6th place.
[Effect of the Invention]
[0006]
According to this invention, the problem in the former can be solved and the suitable multi-permutation pyrimidine for fields including various kinds, such as luminescent material, and its efficient alternative manufacture approach can be offered.
[Best Mode of Carrying Out the Invention]
[0007]
(A multi-permutation pyrimidine and its alternative manufacture approach)
The alternative manufacture approach of the multi-permutation pyrimidine of this invention The inside of two carbon

atoms located in the meta position to this organic radical in the pyrimidine which combined the specific organic radical, Make the first pi electron content compound containing the first pi electron content radical react to the first carbon atom, and this first pi electron content radical is combined (the first pi electron content radical joint process). After making the second pi electron content compound containing the second pi electron content radical react to the second carbon atom and combining this second pi electron content radical (the second pi electron content radical joint process), The process of others which were chosen further suitably if needed is included including what you make the third pi electron content compound which contains the third pi electron content radical for said organic radical react, and is made to permute by this third pi electron content radical (the third pi electron content radical joint process).
The multi-permutation pyrimidine of this invention can be suitably manufactured by the alternative manufacture approach of said multi-permutation pyrimidine of this invention.
Hereafter, the contents of said multi-permutation pyrimidine of this invention are also clarified through explanation of the alternative manufacture approach of the multi-permutation pyrimidine of this invention.
[0008]
- Pyrimidine -
In this invention, the pyrimidine used for a reaction uses what is permuted by the organic radical containing the atom chosen from the 13th group in the long period mold periodic table of an element by the 16th group. This organic radical has combined with said pyrimidine through said atom.
Although chosen from the 13th group in the long period mold periodic table of an element by the 16th group as said atom, also in these, what is chosen from either S atom, Si atom, Se atom, O atom, germanium atom, Sn atom, Pb atom and B atom is desirable, and S atom is more desirable.
Although there is especially no limit and it can choose suitably according to the purpose as a permutation location in said pyrimidine of the organic radical containing said atom, for example, two nitrogen atoms which form a pyrimidine ring are adjoined, and it is desirable that it is the location of the carbon atom of the location of the 2nd place in this pyrimidine ring.
Although there is especially no limit and it can choose suitably as said organic radical according to the purpose, an alkylthio group etc. is mentioned suitably and, specifically, a methylthio radical is mentioned more suitably, for example. These may be used by the one-sort independent and may use two or more sorts together.
[0009]
- The first pi electron content radical joint process -
Said first pi electron content radical joint process is a process which makes the first pi electron content compound containing the first pi electron content radical react to the first carbon atom of the two carbon atoms located in the meta position to said organic radical in said pyrimidine, and combines this first pi electron content radical.
[0010]
Although there is especially no limit and it can choose suitably as said first pi electron content compound according to the purpose if the pi electron content radical is included, the metal salt containing the first pi electron content radical etc. is mentioned suitably, for example.
If it is a radical containing a pi electron as said first pi electron content radical, there will be especially no limit, and it can be suitably chosen according to the purpose, and what may be a univalent radical, and may be a divalent radical, for example, is chosen from an aryl group, a hetero aryl group, an alkenyl radical, and an alkynyl group will be mentioned suitably. These may be used by the one-sort independent and may use two or more sorts together.
[0011]
As said metal salt, there is especially no limit, and it can be suitably chosen according to the purpose, for example, lithium salt etc. is mentioned suitably. In addition, in said first pi electron content radical joint process, in case metals, such as said lithium in said metal salt, combine said first pi electron content radical with a pyrimidine, they function as a catalyst.
[0012]
Also in said first pi electron content radical, what is expressed with either of following structure-expression a-q as a univalent thing about said aryl group is desirable, and what has the joint hand further in the part of the arbitration of a univalent thing expressed with either of following structure-expression a-q is desirable as a divalent thing, for example.

[0013]
[Formula 4]



[0014]
-- Reaction --
It is desirable to be carried out for example, using a catalyst as this reaction at the time of making said first univalent or divalent pi electron content compound react to said first carbon atom.
Although there is especially no limit and it can choose suitably as said catalyst according to the purpose, a metal catalyst etc. is mentioned suitably, for example. These may be used by the one-sort independent and may use two or more sorts together.
[0015]
As said metal catalyst, a lithium catalyst etc. is mentioned suitably, for example. In addition, metals, such as said lithium contained in said first pi electron content compound, can also be used for this metal catalyst as this metal catalyst.
Although there is especially no limit and it can choose suitably as amount of said metal catalyst used according to the purpose, it is about 0.01-10M and 0.1-5M are usually desirable, for example.
[0016]
In this invention, it is desirable to use said not only metal catalyst but further 2, 3-dichloro -5, and the 6-dicyano-1, 4-benzoquinone (DDQ) as a catalyst in the case of said reaction.
Although there is especially no limit and it can choose suitably as said amount of DDQ used according to the purpose, it is about 0.01-10M and 0.1-5M are usually desirable, for example.
[0017]
Although there is especially no limit and it can choose suitably as temperature of said reaction according to the purpose, it is about -20-40 degrees C, and -5-10 degrees C is usually desirable, for example.
[0018]
In addition, this reaction can be performed by carrying out mixing thru/or stirring, etc. in the reaction container suitably chosen from well-known things, and where said alkene compound is dissolved in an organic solvent, it can be performed suitably.
As said organic solvent, there is especially no limit, and it can be suitably chosen according to the purpose, for example, diethylether, dioxane, toluene, a tetrahydrofuran, etc. are mentioned. These may be used by the one-sort independent and may use two or more sorts together. Also in these organic solvents, diethylether, a tetrahydrofuran, etc. are desirable.
[0019]
Said first pi electron content radicals (an aryl group, a hetero aryl group, an alkenyl radical, alkynyl group, etc.) are

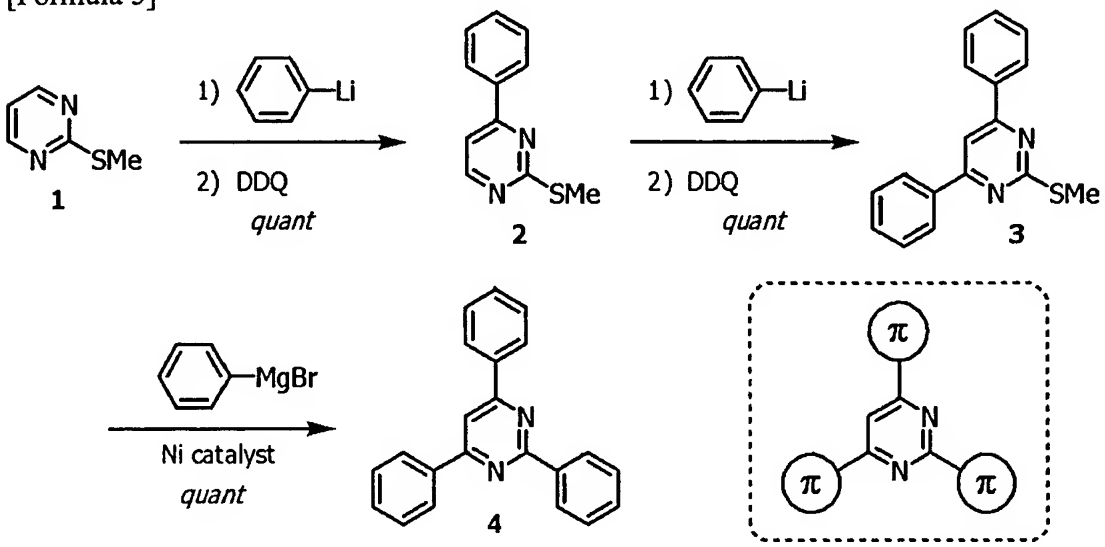
alternatively combined with the first [said] carbon atom located in the meta position to said organic radical in said pyrimidine according to said first pi electron content radical joint process (installation).
[0020]
- The second pi electron content radical joint process -
Said second pi electron content radical joint process is a process which makes the second univalent or divalent pi electron content compound containing the second pi electron content radical react to the second [said] carbon atom located in the meta position to said organic radical in said pyrimidine, and combines this second pi electron content radical.
As said second pi electron content radical, the same thing as said first pi electron content radical is mentioned suitably.
As said second pi electron content compound, the same thing as said first pi electron content compound is mentioned suitably.
In addition, said second pi electron content compound may be the same as said first pi electron content compound, and may differ.
[0021]
As this reaction at the time of making said second univalent or divalent pi electron content compound react to said second carbon atom, the same reaction as said first pi electron content radical joint process and conditions are mentioned suitably. Moreover, this reaction may use a catalyst other than the catalyst used in said first pi electron content radical joint process, and can use suitably the catalyst used in said first pi electron content radical joint process in this second pi electron content radical joint process as it is. Furthermore, this reaction can be performed in the same reaction container as having performed said first pi electron content radical joint process. In this case, the time and effort to which exchange etc. carries out a reaction container, a catalyst, an organic solvent, etc. by Hazama of said first pi electron content radical joint process and this second pi electron content radical joint process is unnecessary, and is efficient, and this case may be called one pot (ONE-POT) processing.
[0022]
Said second pi electron content radical is alternatively combined with the second [said] carbon atom located in the meta position to said organic radical in said pyrimidine according to said second pi electron content radical joint process (installation).
[0023]
The pyrimidine which said first pi electron content radical and said second pi electron content radical combined with the first [said] carbon atom located in the meta position to said organic radical in a pyrimidine and said second carbon atom alternatively, respectively according to the above first pi electron content radical joint process and the second pi electron content radical joint process is obtained.
[0024]
- The third pi electron content radical joint process -
Said third pi electron content radical joint process is a process which makes said organic radical in a pyrimidine permute by this third pi electron content radical using the third univalent or divalent pi electron content compound containing said third pi electron content radical.
[0025]
As said third pi electron content compound, there is especially no limit, and it can be suitably chosen according to the purpose, a univalent or divalent compound is mentioned, and a halogenide, a magnesium content compound, etc. are mentioned especially suitably.
In addition, as said magnesium content compound, the compound expressed with the formula of pi-MgX or XMg-pi-MgX ** is mentioned suitably, for example. Among this type, a univalent pi electron content radical is expressed with the former, a divalent pi electron content radical is expressed with the latter, an aryl group, a hetero aryl group, an alkenyl radical, an alkynyl group, etc. are suitably mentioned by pi, Mg expresses a magnesium atom, and X expresses halogens (a fluorine, chlorine, a bromine, iodine, etc.). Said third pi electron content radical may be the same as said first pi electron content radical and said second pi electron content radical, and may differ.
[0026]
If it is a radical containing a pi electron as said third pi electron content radical, there will be especially no limit, and it can be suitably chosen according to the purpose, and the same thing as said first pi electron content radical and said

second pi electron content radical will be mentioned. These may be used by the one-sort independent and may use two or more sorts together.
[0027]
-- Reaction --
As this reaction at the time of permuting said organic radical by said third pi electron content radical, a cross coupling (Cross-Coupling) reaction is mentioned especially suitably, for example.
Said third pi electron content radical can be made to permute said organic radicals (a silane induction radical, sulfide induction radical, etc.) in this pyrimidine, without attacking said first pi electron content radical combined with said pyrimidine, and said second pi electron content radical according to said first pi electron content radical joint process and said second pi electron content radical joint process according to this cross coupling (Cross-Coupling) reaction.
[0028]
Said cross coupling (Cross-Coupling) reaction For example (a) Okamura H.; Miura, M.; Takei H. Tetrahedron Lett. 1979 43. (b) Wenkert E.; Ferreira T. W.; Michelotti, E. L. Chem. Commun. 1979 637. (c) Luh T.-Y.; nickel Z.-J. Synthesis It is as being indicated by reference, such as 1990 and 89.
[0029]
As for especially a limit, as conditions for said cross coupling (Cross-Coupling) reaction, it is desirable for there to be nothing, and to be able to choose suitably according to the purpose, for example, to be carried out under existence of a transition metal catalyst.
Although there is especially no limit and it can choose suitably as said transition metal catalyst according to the purpose, a nickel catalyst is mentioned suitably, for example. These may be used by the one-sort independent and may use two or more sorts together. Also in said nickel catalyst, especially nickel salt of NiCl2 grade is desirable.
Although there is especially no limit and it can choose suitably as amount of said transition metal catalyst used according to the purpose, for example, it is usually less than [20 mol %], and less than [10 mol %] is desirable, and 3-7-mol % is more desirable.
[0030]
Although there is especially no limit and it can choose suitably according to the purpose as temperature of the cross coupling (Cross-Coupling) reaction in said third pi electron content radical joint process, it is about 40-120 degrees C, and 50-100 degrees C is desirable, and 45 degrees C or more less than 75 degrees C are usually more desirable, for example.
[0031]
In addition, this reaction can be performed by carrying out mixing thru/or stirring, etc. in the reaction container suitably chosen from well-known things, and can be suitably performed in the reaction mixture which performed said second pi electron content radical joint process.
As said organic solvent, there is especially no limit, and it can be suitably chosen according to the purpose, for example, dioxane, toluene, a tetrahydrofuran, etc. are mentioned. These may be used by the one-sort independent and may use two or more sorts together. Also in these organic solvents, toluene, a tetrahydrofuran, etc. are desirable.
[0032]
According to said third pi electron content radical joint process, said organic radical in said pyrimidine is alternatively permuted by said third pi electron content radical (installation).
[0033]
Said organic radical in said pyrimidine is alternatively permuted by said third pi electron content radical by the above-mentioned third pi electron content radical joint process, and the multi-permutation pyrimidine of this invention is alternatively compounded.
[0034]
In the alternative manufacture approach of the multi-permutation pyrimidine of this invention A phenyl lithium and said DDQ are used as shown in the following scheme. According to said first pi electron content radical joint process and the second pi electron content radical joint process which made the phenyl group said first pi electron content radical and said second pi electron content radical, and made a lithium and said DDQ the catalyst In the first [said] carbon atom located in the meta position to said organic radical in a pyrimidine, and said second carbon atom Said first pi electron content radical and said second pi electron content radical permute alternatively, respectively (introduced).

Using a phenyl magnesium bromide and nickel salt according to for example, said third pi electron content radical joint process which made the phenyl group said third pi electron content radical, and made nickel the catalyst Said organic radical is alternatively permuted by said third pi electron content radical, and the multi-permutation pyrimidine of this invention is compounded alternatively. In addition, said first pi electron content radical and said second pi electron content radical can be performed by the one pot (ONE-POT) processing mentioned above. In this case, the multi-permutation pyrimidine of this invention is compoundable in effectiveness.

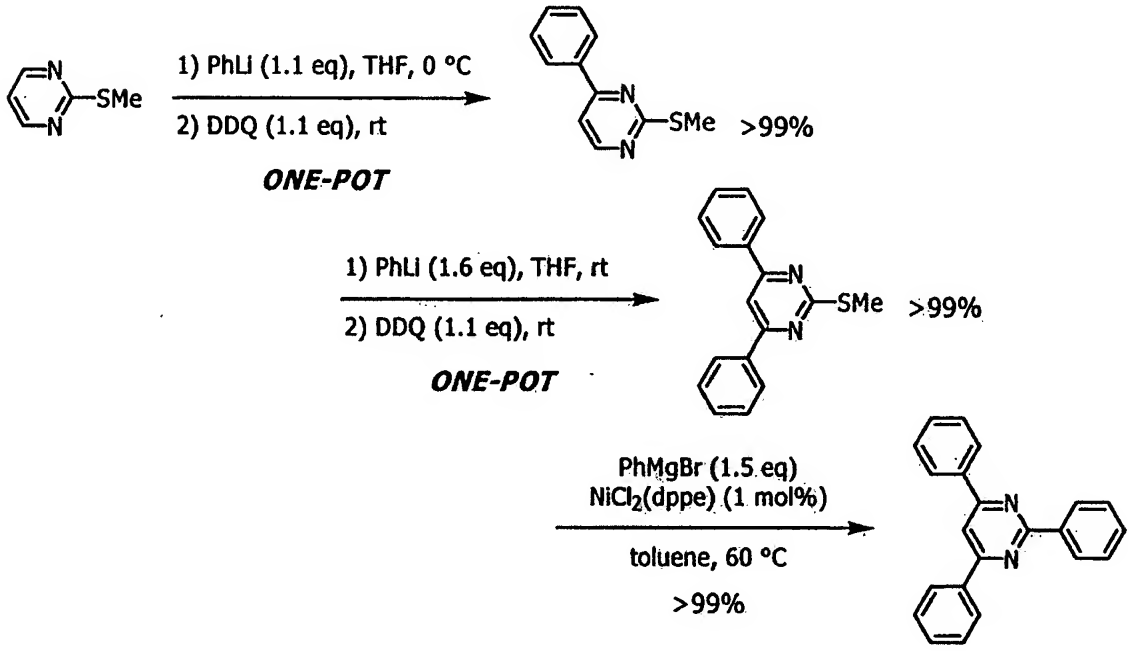
[0035]

[Formula 5]



[0036]

[Formula 6]



[0037]

In the alternative manufacture approach of the multi-permutation pyrimidine of above-mentioned this invention (1) The

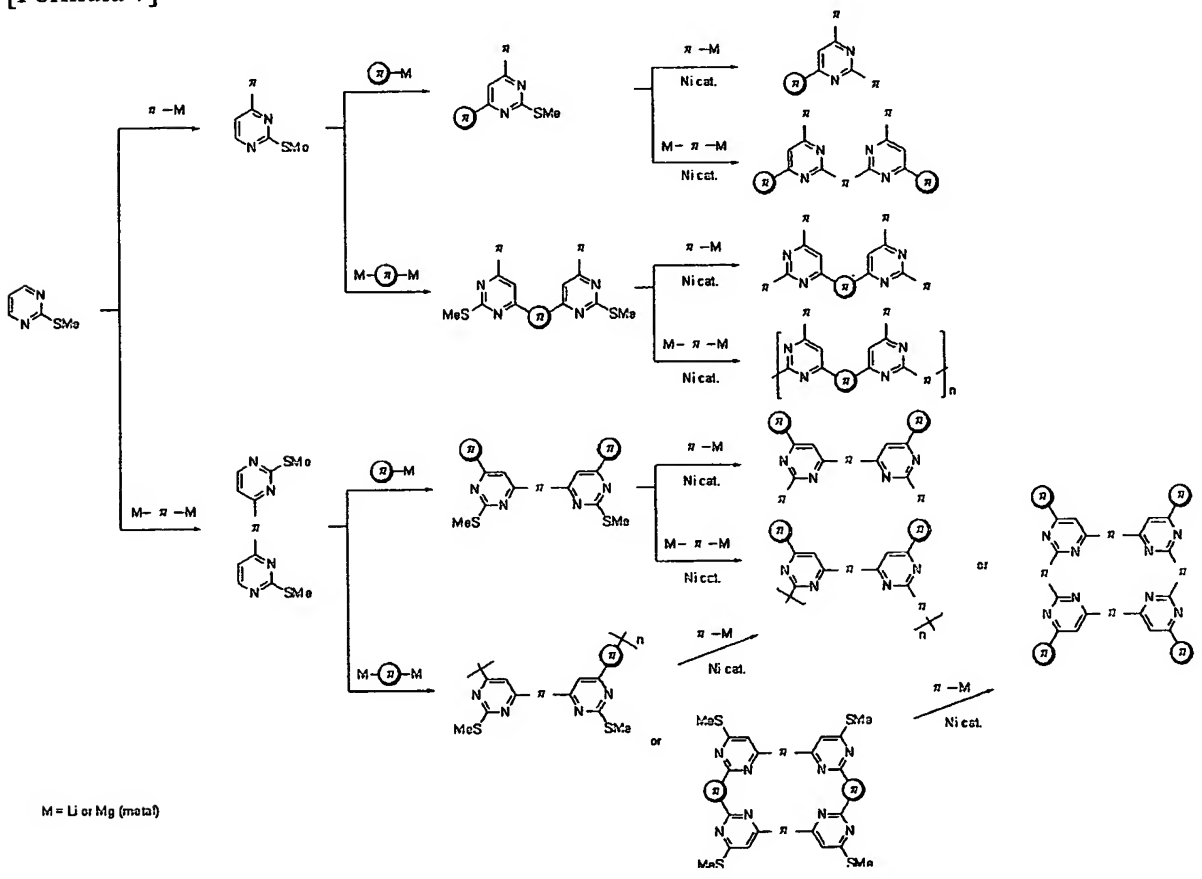
mode the first pi electron content compound, the second pi electron content compound, and whose third pi electron content compound are univalent compounds (stage of the top of the following reaction scheme), (2) The first pi electron content compound and the second pi electron content compound are univalent compounds. The mode whose third pi electron content compound is a divalent compound (from the following reaction scheme to the 2nd stage), (3) The first pi electron content compound and the third pi electron content compound are univalent compounds. The mode whose second pi electron content compound is a divalent compound (from the following reaction scheme to the 3rd stage), (4) The mode the second pi electron content compound and whose third pi electron content compound the first pi electron content compound is a univalent compound, and are divalent compounds (from the following reaction scheme to the 4th stage), (5) The mode the second pi electron content compound and whose third pi electron content compound the first pi electron content compound is a divalent aryl compound, and are univalent aryl compounds (from the following reaction scheme to the 5th stage), (6) The first pi electron content compound and the third pi electron content compound are divalent aryl compounds. The mode whose second pi electron content compound is a univalent aryl compound (from the following reaction scheme to the 6th stage), a list -- (7) -- mode (6th [from the following reaction scheme] and 7th stage) ** whose third pi electron content compound the first pi electron content compound and the second pi electron content compound are divalent aryl compounds, and is a univalent aryl compound is desirable.

[0038]

The multi-permutation pyrimidine manufactured in these desirable modes has the structure where the carbon atom of the 2nd place in a pyrimidine ring, the 4th place, and the 6th place was permuted by the pi electron content radical, and has one structure of the structures shown in the right-hand side of the following scheme by the reaction expressed with the following scheme.

[0039]

[Formula 7]



However, n expresses polymerization degree during the above and pi expresses pi electron content radicals (an aryl group, a hetero aryl group, an alkenyl radical, alkynyl group, etc.).

[0040]

According to the alternative manufacture approach of the multi-permutation pyrimidine of this invention, said first pi electron content radical and said second pi electron content radical It can be made to combine with the first [said] carbon atom located in the meta position to said organic radical, and said second carbon atom respectively alternatively and efficiently (permutation). Said organic radical can permute said third pi electron content radical alternatively and efficiently, and the multi-permutation pyrimidine which has desired structure can be manufactured alternatively and efficiently.

[0041]

Said multi-permutation pyrimidine of this invention manufactured by the alternative manufacture approach of said multi-permutation pyrimidine of this invention can be especially used suitably as a luminescent material, although it is suitably usable in various fields.

[Example]

[0042]

Hereafter, although the example of this invention is explained, this invention is not limited to this example at all.

[0043]

(Example 1)

As it was the following, the multi-permutation pyrimidine was compounded alternatively.

- The first pi electron content radical joint process -

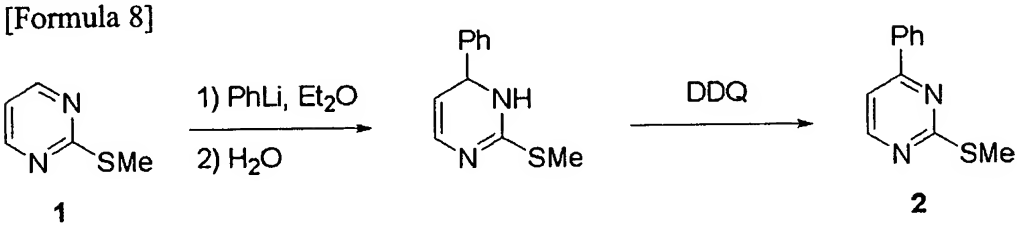
the following as a raw material -- phenyl lithium 0.525mmol (0.93M cyclohexane ether solution) as said first pi electron content compound was dropped at 0 degree C to 2-methylthio pyrimidine 63.6mg (0.50mmol) diethylether solution 1.5mL expressed with 1. In addition, the phenyl group in said phenyl lithium is said first pi electron content radical, and said lithium functions as said catalyst. After stirring at 0 degree C for 1 hour, H2O (1mL) was added to the reaction solution. Mixture was extracted by CHCl3 (1mLx4), and the organic layer was dried by MgSO4. The organic layer was condensed and the rough product of an adduct was obtained. This was melted to the tetrahydrofuran (1.5mL), H2O (1.5mL) and an acetic acid (14mL) were added to the solution, and 2, 3-dichloro -5, and a 6-dicyano-1, 4-benzoquinone (DDQ) 116.3mg (0.51mmol) tetrahydrofuran (1.5mL) solution were added further. After stirring for 15 minutes at a room temperature, the NaOH water solution (0.18mL) of 3M and H2O (10mL) were added to mixture. Mixture was extracted by diethylether (10mLx3) and the organic layer was dried by MgSO4. The rough product was obtained by condensing an organic layer. silica gel chromatography - the following -- 101.2mg (yield: >99%) of pyrimidine compounds expressed with 2 was obtained as a white solid-state.

[0044]

The obtained pyrimidine compound has the structure which the phenyl group permuted by the first carbon atom (the 4th place) in a pyrimidine ring located in the meta position to the methylthio radical as said organic radical. The 1H The analysis value of NMR (400 MHz, CDCl3) delta 2.65 (s, 3H) 7.36 (d, J = 5.2 Hz, 1H) 7.45-7.52 (m, 3H) 8.05-8.10 (m, 2H) 8.53 (d, J = 5.2 Hz, 2H) it is -- 13C The analysis value of NMR (100MHz, CDCl3) delta14.4 111.8 127.0 128.8 131.0 136.2 157.4 163.6 It was 172.6.

[0045]

[Formula 8]



1 2

[0046]

- The second pi electron content radical joint process -

next, the following -- phenyl lithium 0.40mmol (0.87M cyclohexane ether solution) was dropped at 0 degree C to 2-

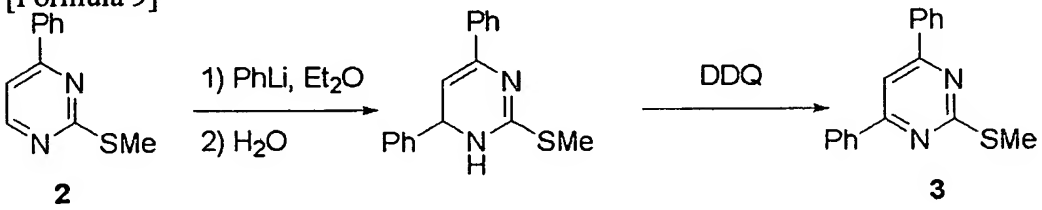
methylthio-4-phenyl pyrimidine 49.4mg (0.24mmol) tetrahydrofuran solution 1.0mL expressed with 2. After stirring at a room temperature for 4 hours, acetic-acid 23mL and H2O1.0mL were added to the reaction solution, and further 2, 3-dichloro -5, and 6-dicyano-1, 4-benzoquinone (DDQ) 61.6mg (0.27mmol) tetrahydrofuran solution 1.0mL was added. After stirring for 45 minutes at a room temperature, NaOH water-solution 0.17mL of 3M was added to mixture. Ethyl acetate extracted mixture (1mLx3) and the organic layer was dried by MgSO4. The rough product was obtained by condensing an organic layer. silica gel chromatography - the following -- 67.9mg (yield: >99%) of pyrimidine compounds expressed with 3 was obtained as a white solid-state.

[0047]

The obtained pyrimidine compound has the structure which the phenyl group permuted by the second carbon atom (the 6th place) in a pyrimidine ring located in the meta position to the methylthio radical as said organic radical. The 1H The analysis value of NMR (400MHz, CDCl3) delta 2.72 (s, 3H) 7.50-7.52 (m, 6H) 7.77 (s, 1H) 8.10-8.16 (m, 4H) it is -- 13C NMR (100MHz, CDCl3) delta14.5 107.8 127.1 128.7 130.8 136.8 164.5 It was 172.6.

[0048]

[Formula 9]



[0049]

- The third pi electron content radical joint process -

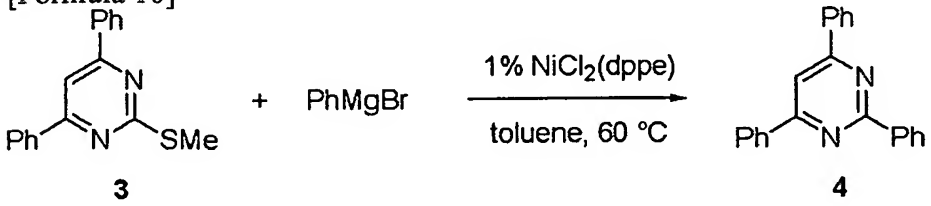
next, the following -- phenyl MgBr0.30mmol (2.94M tetrahydrofuran solution) was added to toluene solution 1.0mL (2-methylthio [which is expressed with 3] -4, and 6-diphenyl pyrimidine 53.8mg (0.19mmol), and NiCl2 (dppe)1.1mg (2.08micromol, 1%)). In addition, the phenyl group in this phenyl MgBr is said third pi electron content radical. After stirring a toluene solution at 60 degrees C for 14 hours, it returned to the room temperature, 1-N HCl1.0mL was added, and the sodium hydrogencarbonate neutralized after that. Ethyl acetate extracted mixture (2mLx3) and the organic layer was dried by MgSO4. silica gel chromatography [after obtaining a rough product by condensing an organic layer] - the following -- multi-permutation pyrimidine 58.5mg (yield: >99%) expressed with 4 was obtained as a white solid-state.

[0050]

Said organic radical [in / in the obtained pyrimidine compound / a pyrimidine ring] is permuted by the phenyl group (carbon atom location of the 2nd place). It has the structure of 2, 4, and 6-triphenyl pyrimidine, and is the 1H. The analysis value of NMR (400 MHz, CDCl3) delta7.50-7.60 (m, 9H) 8.02 (s, 1H) 8.25-8.35 (m, 4H) 8.70-8.80 (m, 2H) it is -- 13C NMR (100MHz, CDCl3) delta110.2 127.1 128.3 128.4 128.8 130.5 130.6 137.4 138.0 164.3 It was 164.5.

[0051]

[Formula 10]



[0052]

(Example 2)

As it was the following, the multi-permutation pyrimidine was compounded alternatively.

- The first pi electron content radical joint process -

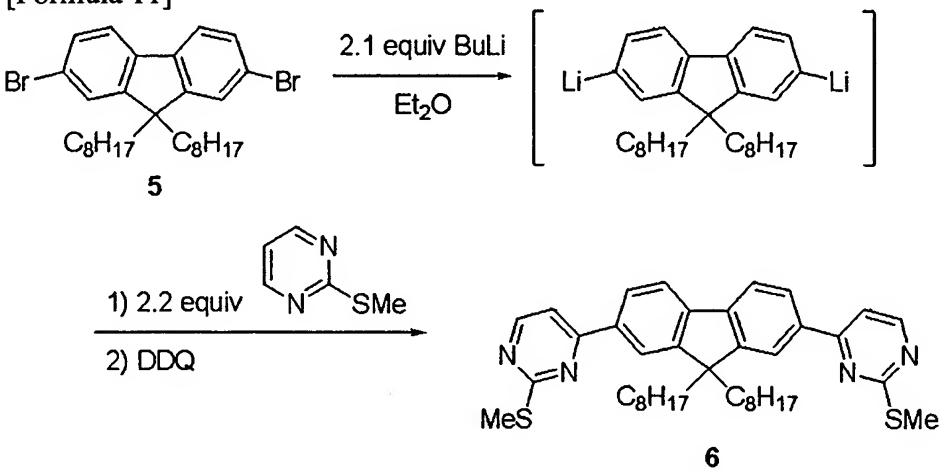
the following as a raw material -- BuLi0.315mmol (1.52M hexane solution) was dropped at -78 degree C to ant-RUJIBUROMIDO 82.7mg (0.151mmol) diethylether solution 1.5mL expressed with 5. - After stirring for 30 minutes at a room temperature for 30 minutes by 78 degrees C, 2-methylthio pyrimidine 41.6mg (0.33mmol) was dropped at -78 degree C. It is [acetic-acid 20L and] H2O to the reaction solution after stirring at a room temperature by 0 degree C for 3 hours for 1 hour. The mixed solution with 1mL was added. On the other hand, 2, 3-dichloro -5, and a 6-dicyano-1, 4-benzoquinone (DDQ) 74.9mg (0.33mmol) tetrahydrofuran (1.0mL) solution were added, and it stirred for 30 minutes at the room temperature. 3M A NaOH water solution (0.2mL) and after adding H2O (10mL), mixture was extracted by CHCl3 (2mLx3), and the organic layer was dried by MgSO4. if an organic layer is condensed and silica gel chromatography - refines the rough product of an adduct -- the following -- 59.4mg (59% of yield) of pyrimidine compounds expressed with 6 was obtained.

[0053]

Pyrimidine compound 1H obtained The analysis value of NMR (400MHz, CDCl3) delta0.60-0.70 (m, 4H) 0.77 (t, J = 6.8 Hz, 6H) 1.00-1.20 (m, 20H) 2.05-2.12 (m, 4H) 2.68 (s, 6H) 7.44 (d, J = 5.2 Hz, 2H) 7.84 (d, J = 8.0 Hz, 2H) 8.09 (s, 2H) 8.12 (d, J = 8.0 Hz, 2H) 8.55 (d, J = 5.2 Hz, 2H) it was .

[0054]

[Formula 11]



[0055]

- The second pi electron content radical joint process -

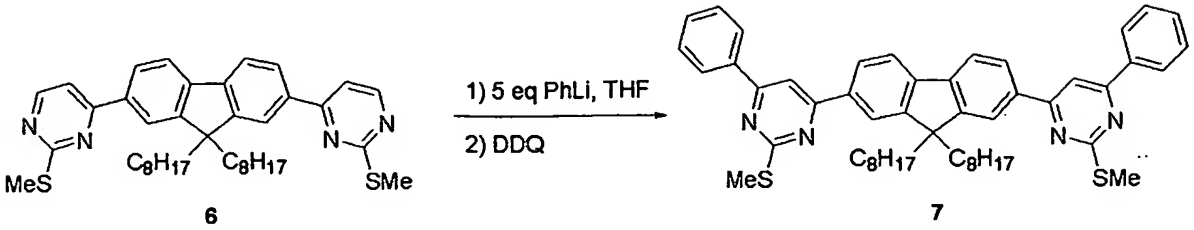
next, the obtained following -- phenyl lithium (PhLi) 0.40mmol (a 0.92M cyclohexane / ether solution) was dropped at -78 degree C to the tetrahydrofuran (1.5mL) solution of 51.1mg of pyrimidine compounds expressed with 6 (0.08mmol). After stirring at a room temperature by 0 degree C for 2 hours for 1 hour, the acetic acid (40microL) and the mixed solution with H2O (2mL) were added to the reaction solution. On the other hand, the 2, 3-dichloro -5, and 6-dichloro-1, 4-benzoquinone (DDQ) 40.0mg (0.18mmol) tetrahydrofuran (2.0mL) solution was added, and it stirred for 30 minutes at the room temperature. 3M A NaOH water solution (0.2mL) and after adding H2O (10mL), mixture was extracted by CHCl3 (2mLx3), and the organic layer was dried by MgSO4. if an organic layer is condensed and silica gel chromatography - refines the rough product of an adduct -- the following -- 35.8mg (75% of yield) of pyrimidine compounds expressed with 7 was obtained.

[0056]

Pyrimidine compound 1H obtained The analysis value of NMR (400MHz, CDCl3) delta0.65-0.75 (m, 4H) 0.76 (t, J = 6.8 Hz, 6H) 1.00-1.20 (m, 20H) 2.05-2.10 (m, 4H) 2.76 (s, 6H) 7.50-7.55 (m, 6H) 7.83 (s, 2H) 7.87 (d, J = 8.4 Hz, 2H) 8.15-8.20 (m, 8H) it was .

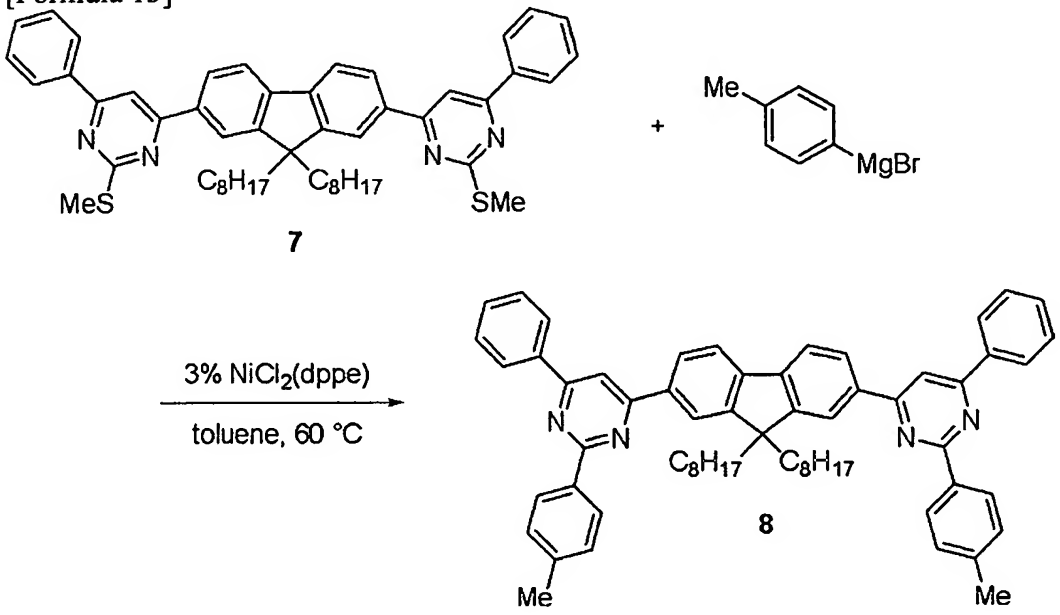
[0057]

[Formula 12]



6 7

[0058]
- The third pi electron content radical joint process -
the obtained following -- 2-tolyl magnesium bromide 0.30mmol (1.0M tetrahydrofuran solution) was added to 34.0mg (0.06mmol) of pyrimidine compounds expressed with 7, and a NiCl2 (dppe)1.0mg (1.8micromol) toluene (1.5mL) solution. After stirring a solution at 60 degrees C for 24 hours, it returns to a room temperature, and it is 1N. HCl (1.0mL) was added and the sodium hydrogencarbonate neutralized after that. Chloroform extracted mixture (4mLx3) and the organic layer was dried by MgSO4. if a rough product is obtained by condensing an organic layer and silica gel chromatography - refines -- the following -- multi-permutation pyrimidine (three substitution products) 37.8mg (yield: >99%) expressed with 8 was obtained.
[0059]
Pyrimidine compound 1H obtained The analysis value of NMR (400MHz, CDCl3) delta0.70-0.85 (m, 10H) 1.05-1.10 (m, 20H) 2.18-2.25 (m, 4H) 2.47 (s, 6H) 7.36 (d, J = 8.2 Hz, 4H) 7.50-7.60 (m, 6H) 7.93 (d, J = 7.6 Hz, 2H) 8.04 (s, 2H) 8.25-8.35 (m, 8H) 8.64 (d, J = 8.0 Hz, 4H) it was . Moreover, 13C The analysis value of NMR (100MHz, CDCl3) 14. 1 21.7 22.7, 24.1 29.3 29.4, 30.1 31.9 40.4, 55.7 110.1 120.5, 121.6 126.5 127.2, 128.3 128.8 129.1 130.5 135.4 137.0 137.7 140.7 142.9 152.1 164.4 164.5 It was 164.6.
[0060]
[Formula 13]



7 8

[Availability on industry]
[0061]
The multi-permutation pyrimidine of this invention is usable in for example, various fields, and can be suitably used as a luminescent material etc.
The alternative manufacture approach of the multi-permutation pyrimidine of this invention can make a desired pi electron content radical permute by the 2nd place, the 4th place, and the 6th place alternatively and efficiently, and is

usable suitable for alternative and efficient manufacture of the suitable multi-permutation pyrimidine for luminescent material etc.

[Translation done.]